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October 16, 1989

Mr. Bernard Schorle
Remedial Project Manager
U.S. Environmental Protection Agency
Region V, Mail Stop 5HS-11
230 S. Dearborn Street
Chicago, IL 60604

Dear Bernard:

As per our phone conversation on October 13, I have a number of comments concerning technical matters at the Pagel's Pit site:

1. Warzyn's contention that the levels of volatile organic compounds (VOC's) which have been measured in the landfill leachate are representative of past levels may be incorrect. If it is assumed that no VOC's have been emplaced at any point in the landfill after that area has been filled, or that significant quantities of VOC's were not emplaced anywhere in the landfill after some specific cut off time, there is no mechanism for adding significant quantities of VOC's to the landfill leachate. There are, however, a number of potential mechanisms for decreasing the concentration of VOC's in the leachate after they have been emplaced. Among the possibilities are:
 - a. Degradation of polychlorinated ethenes, ethanes, and other VOC's. The work of a number of researchers (Vogel, and McCarty, Applied and Environmental Microbiology, May 1985, p. 1080-1083; Bouwer and McCarty, Applied and Environmental Microbiology, April 1983, p. 1286-1294) has shown that tetrachloroethylene and tetrachloroethane can be at least partially transformed by reductive dehalogenation to carbon dioxide under reducing and/or methanogenic conditions over a period of days. Several other studies have indicated that a variety of VOC's can be biodegraded under reducing and/or methanogenic conditions to form carbon dioxide (Wilson and others, Environmental Science and Technology, 1986, v. 20, p. 997-1002). Abiotic degradation of certain VOC's has also been shown to occur.
 - b. Extraction with liquid leachate. The landfill has an extensive system designed for the removal of liquid leachate via pumping. Warzyn has also noted that there is a plume of liquid migrating from the landfill. Regardless of the fate of the dissolved VOC's once the leachate leaves the landfill, any water which leaves the landfill by whatever means can be expected to take dissolved VOC's with it.

- c. Volatilization to the atmosphere. Any body of water which contains dissolved VOC's and is in contact with the atmosphere will lose volatiles to the atmosphere. I have enclosed an article which may further explain these processes (Thibodeaux and others, Journal of Hazardous Materials, 1982, v. 7, p. 63-74).
 - d. Dilution. If it is assumed that the majority of the VOC's are/were located in one part of the landfill, it seems reasonable to suggest that, as the volume of water in the landfill increased as the landfill was filled in, VOC concentrations decreased when the older, more highly contaminated water mixed with the younger, comparatively clean water.
 - e. Migration with the observed release of methane and carbon dioxide. My preliminary discussions with USGS personnel who research gas migration in the unsaturated zone have lead me to believe that is at least possible to have VOC's moving with the methane.
2. Warzyn's statements concerning DCE concentrations in well B16 in January of 1985 should be regarded with some caution. Warzyn's report titled "Supplemental Investigation: Winnebago Reclamation Landfill, Rockford, Illinois" which is dated March 5, 1985 indicates that the measured DCE concentration in well B16 was 39 ug/l on December 27, 1984 and 220 ug/l on January 2, 1985. It is difficult to conceptualize any combination of chemical and hydraulic factors which would be realistic for this aquifer that could result in such a large increase in concentration in such a short period of time. It seems likely, therefore, that one of the reported values is incorrect. Because previous reports have indicated that the DCE concentration in well B16 ranges from approximately 7 to 29 ug/l, it seems more likely that the lower value is accurate. If Warzyn continues to maintain that the DCE concentration is actually 220 ug/l, they should explain this discrepancy and support the explanation with data.
3. Drillers logs for wells G108 and G110 indicate that methane was detected when these wells were being drilled in late 1984, over 4 years after the installation of the leachate-and methane-collection systems in the landfill. This would seem to indicate that landfill gasses are/were released from the landfill after installation of the methane-extraction system or that landfill gasses may remain in the ground for extended periods of time after the instalation of the methane-extraction system.

Drillers logs for wells G109A, B16A, and G110 indicate that VOC's were detected when these wells were being drilled in late 1984. The presence of material described as having a solvent odor above the water table in well G109A and the indication of VOC's well above the water table in well G110 may indicate the presence of a VOC source in the southeast corner. These logs are presented in Appendix C of the previously cited Warzyn report.

4. Warzyn may wish to consider the effect of methane and carbon dioxide gas migration on alkalinity and pH values in the ground water in the vicinity of the landfill. Carbon dioxide gas has the potential to react with water to form carbonic acid ($\text{CO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3(\text{aq})$) and/or bicarbonate and hydrogen ion ($\text{CO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$). While reactions in the carbonate system are quite complex, it is possible to increase the alkalinity and decrease the pH of ground water by releasing $\text{CO}_2(\text{g})$ from the landfill. It may not be necessary, therefore, to explain the comparatively high alkalinity and low pH of the ground water in the vicinity of the southeast corner of the landfill by contamination from upgradient water.
5. The draft E.C. Jordan report titled "Data Analysis and Summary Report for Deep Groundwater Assessment ACME Solvents Superfund Site" dated Jan. 1986 shows the presence of high levels of acetone, isopropanol, methyl isobutyl ketone, and methylene chloride in the ground water. It may be of value to use one or more of these compounds as a tracer of contamination from the ACME site in future sampling rounds. Although there is some doubt as to the accuracy of these numbers, and there are a number of potential problems with this technique, finding significant concentrations of one or more of these compounds (particularly methyl isobutyl ketone) could indicate that ground water in the vicinity of the Pagel's site contains compounds derived from the ACME site.
6. Warzyn's hypothesis that one of the reasons for the relatively small amount of observed contamination between the ACME and Pagel's sites is the relatively poor degree of hydraulic connection between the screened interval of these wells and the fractures in the aquifer may require further explanation. If slug testing does indicate that the wells between the sites are in comparatively poor hydraulic connection with the fractures in the aquifer, Warzyn will finally have some data to support this hypothesis. However, it is important to keep in mind that this appears to be a double-porosity aquifer. In a double-porosity aquifer, diffusion of water and contaminant into the rock matrix can be expected to have a significant influence on contaminant distribution. Warzyn should explain why they seem to consider diffusion to be a relatively unimportant mechanism for contaminant migration in this aquifer.

Feel free to call me at FTS 958-5368 with any further questions or comments.


Robert Kay
Hydrologist

cc. Novitzki
Mills

MODELS OF MECHANISMS FOR THE VAPOR PHASE EMISSION OF HAZARDOUS CHEMICALS FROM LANDFILLS*

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Summary

Quantities of hazardous chemicals have been placed in sanitary landfills in conjunction with solid waste. This paper presents three vapor phase transport mechanisms: molecular diffusion, bio-gas convection, and barometric pressure pumping. These mechanisms are incorporated into a dynamic model that simulates the emission flux rate of chemicals, as a function of landfill and environmental variables. The simulation model is driven by time-varying atmospheric pressure fluctuations. Darcy's law is used to simulate gas movement through the landfill cap material to and from the landfill cells. With all mechanisms operative, a rate of 290 g benzene/m² d was obtained from the model using benzene as a test chemical. Atmospheric pressure fluctuations pump toxic vapors and gases from the storage cells of hazardous waste landfills to the air above. This pumping enhances the vapor phase molecular diffusion process. The calculated benzene flux rate with diffusion and atmosphere pumping was 13 g/m² d. Uncertainties and limitations of the model are considered which include: vapor and gas circulation in and between cells, adsorption onto solids and multi-cell landfills. The model presented is a practical tool for initial evaluation studies of volatile chemical emissions from landfills and provides a basis upon which to construct more realistic simulation models.

Introduction

Hazardous chemicals placed in near-surface impoundments such as landfills, burial trenches or pits, and similar subterranean enclosures can move out of these sites by transport processes in both the gaseous and aqueous phases. It is important to quantify the movement rate of these substances in order to assess the hazards associated with the exposure of selected biota, including man. Chemical transport from such sites via the water route is a fairly well known process and a wealth of empirical evidence and verified analytical models exist to aid in predicting concentration levels in water aquifers. In contrast, little information exists on the gas phase transport processes from near-surface impoundments.

*This paper was presented at a Symposium on Toxic Substances Management Programs, Division of Chemical Health and Safety, 181st American Chemical Society National Meeting, Atlanta, Georgia (U.S.A.), March 29-April 3, 1981.

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The detection of volatile chemical species in air at or around landfills has been reported. The only field measurements of emission rates known to the author were performed by Lu and Matuszek [1]. The work involved the movement of tritiated compounds from buried radioactive waste. Hexachlorobenzene was present in the air nearby a hazardous waste landfill in Louisiana. Farmer, Yang and Letey [2] measured hexachlorobenzene flux rates from a laboratory scale landfill simulator. Alzaydi, Moore and Rao [3] have done extensive modelling work with the diffusive transport of methane and other simple gas molecules from conventional solid waste landfills. Thibodeaux [4] developed a steady-state model that accounts for diffusive transport and bio-gas convective transport of hazardous chemical species from landfill cells. Vinyl chloride, benzene, chloroform and a polychlorinated biphenyl were used in emission rate calculations. The model did not account for atmospheric pumping out-gassing of the cells.

The purpose of this paper is to unify the known mechanisms for the transport of chemical vapors from such sites and to develop realistic prediction models. The dominant mechanisms are gas phase molecular diffusion, biogas venting, and barometric pressure pumping. Results of model calculations based on reasonable scenarios of chemicals existing in near-surface impoundments, will be used to quantify the magnitude of the gas phase transport rates and to reveal the interactions and relative contributions of the various mechanisms.

Transport in porous media

The environment of concern is porous media. The chemical species of concern originate in cells which consist chiefly of solid or semi-solid waste which is porous. The individual landfill cell partitions and the cap consist of a soil-clay material which is also porous.

Gasflow

For the flow of a fluid through a porous medium, the equation of continuity (modified for gas generation; r_g) and motion (Bird et al. [5]) are

$$\epsilon \frac{\partial \rho}{\partial L} = -(\bar{\nabla} \cdot \rho \bar{v}) + r_g$$

and

$$\bar{v} = -\frac{K}{\mu} (\bar{\nabla} p - \rho \bar{g})$$

the latter being Darcy's law, where ϵ is the porosity and K is the permeability of the porous medium. The velocity \bar{v} in these equations is the superficial velocity (volume rate of flow through a unit cross-sectional area of the solid plus fluid) averaged over a small region of space — small with respect

Fig. 1.

to macroscopic pore size and flow time.

The basis for chemical concentration is (g/cm^3) .

$$\epsilon \frac{d\rho}{dt}$$

where ϵ is the superficial porosity, h_c is the capillary height, and f is the flow time.

$$u = \frac{K}{\mu L}$$

where μ is the cell gas viscosity, and eqns (3) and (4) are

$$\epsilon \frac{d\rho}{dt} =$$

the dynamic pressure.

Chemical species. The gas is described by the equation of state.

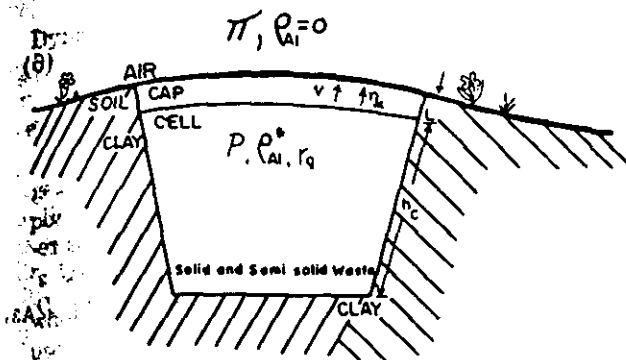


Fig. 1. Idealized single-cell landfill.

to macroscopic dimensions in the flow system but large with respect to the pore size. The quantities ρ and p are averaged over a region available to flow that is large with respect to the pore size.

The idealized single-cell landfill depicted in Fig. 1 will be used as the basis for the model. The gradientless cell region will be a uniform source of chemical A of concentration ρ_{Ai}^* (g/cm³), and biogas production rate r_g (g/cm³ s). The equation of continuity simplifies to:

$$e_c \frac{d\rho}{dt} = -\frac{\rho v}{h_c} + r_g \quad (3)$$

where e_c is cell porosity, ρ is cell gas density (g/cm³), t is time (s), v is superficial velocity (positive outward) through the landfill cap (cm/s), and h_c is cell depth (cm). It is customary to neglect the gravity term since it is small for gases with respect to the pressure term so that for one-dimensional flow through the cap eqn (2) simplifies to:

$$v = \frac{K}{\mu L} (p - \pi) \quad (4)$$

where K is the permeability of the cap material in darcys (cm² cp/s atm), μ is cell gas viscosity (cp) (centipoise), L is the cap thickness (cm), P is cell gas pressure (atm), and π is atmospheric pressure (atm). Combining eqns (3) and (4) yields:

$$e_c \frac{d\rho}{dt} = -\frac{\rho K}{h_c \mu L} (p - \pi) + r_g \quad (5)$$

the dynamic behavior of the cell gas density as a function of atmospheric pressure fluctuations and biogas generation.

Chemical vapor transport

The gaseous transport of chemical vapors through the porous cap is described by the continuity equation for species A in the pore volume:

$$\bar{v} \cdot \bar{v} \rho_{A1} + \frac{\partial \rho_{A1}}{\partial L} = \bar{v} \cdot D_{A3} \bar{v} \rho_{A1} + r_A \quad (6)$$

where ρ_{A1} is the mass concentration of chemical A (g/cm^3), $\bar{v}' = \bar{v}/\epsilon$ is the velocity in the pore spaces (cm/s), D_{A3} is the diffusion coefficient for chemical A in the cap material (cm^2/s), and r_A is rate of reaction of A ($\text{g}/\text{cm}^3 \text{ s}$). It will be assumed that pore space capacity of the cap is small compared to that of the cell so that the gas flow and diffusion process respond very quickly and are at steady state. For a unidirectional process with negligible reaction (or absorption in the pore spaces) and constant D_{A3} , eqn (6) simplifies to:

$$v \frac{d\rho_{A1}}{dy} = D_{A3} \frac{d^2 \rho_{A1}}{dy^2} \quad (7)$$

Upon integration, this model yields the following expression for the flux rate n_A , ($\text{g}/\text{cm}^2 \text{ s}$), through the cap material (Thibodeaux [4])

$$n_A = \frac{D_{A3}}{L} \rho_{A1}^* \left(\frac{R \exp R}{\exp R - 1} \right) \quad (8)$$

where $R = Lv/D_{A3}$, and L is the thickness of the cap (cm). It should be noted that due to changes in barometric pressure, π , the velocity, in the cap material, and correspondingly R , can be positive, zero or negative. In the case of $R = 0$, $n_A = D_{A3} \rho_{A1}^*/L$. Figure 2 shows the general behavior of the bracket term in eqn (8) as a function of R . For large positive R velocity controls the flux rate and for large negative R it essentially stops the flux of chemical A through the cap.

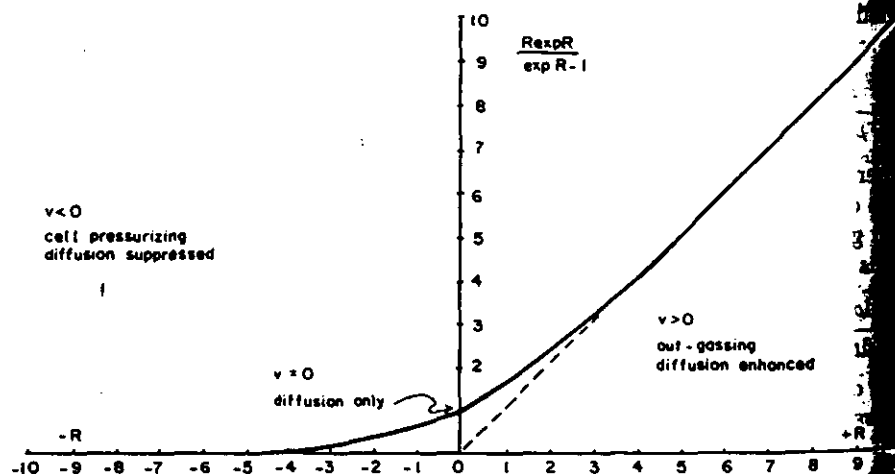


Fig. 2. Diffusion-velocity parameter.

Dynamic :

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$$r_g = r_B \rho_w$$

where ρ_w use of the eqn. (5), i

$$\frac{dp}{dt} = \frac{r_B \rho_w}{\epsilon_c}$$

where p is

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Dynamic simulation model

In order to better understand the mechanisms controlling vapor transport from subterranean chemical burial chambers, a dynamic simulation model was constructed that displayed the major features of the system. Biogas generation rates are typically reported as gas volume per unit solid waste per time, r_B ($\text{cm}^3/\text{g s}$) so that r_g in eqn. (5) becomes:

$$r_g = r_B \rho_w \rho \quad (9)$$

where ρ_w is the bulk density of the waste material in the cell (g/cm^3). By use of the ideal gas law and eqn. (9) the reduced continuity equation, eqn. (5), is transformed to:

$$\frac{dp}{dt} = \frac{r_B \rho_w p}{\epsilon_c} - \frac{Kp(p - \pi)}{\epsilon_c h_c L \mu} \quad (10)$$

where p is in atmospheres.

It is apparent from eqn. (10) that the fluctuating atmospheric pressure (i.e., $\pi(t)$) will influence cell pressure p in a non-linear fashion. The biogas generation rate r_B will also affect cell pressure. For the case of $r_B = 0$, a cyclic atmospheric pressure variation can cause a cyclic effect on cell pressure, which lags with a time constant $h_c \epsilon_c L \mu / Kp$. During the cycling period when $p < \pi$; $v' < 0$ (air inflow) and when $p > \pi$; $v' > 0$ (gas venting), as can be seen from eqn. (4). Therefore a cycling atmospheric pressure can cause periods of pressurization of the cell biogas followed by periods of out-gassing. Lu and Matuszek [1] observed this effect through a trench cover from buried radioactive waste. During pressurization R also becomes negative and n_A is suppressed (see Fig. 2). During out-gassing R is positive and can increase the flux rate greatly. A numerical simulation can be performed to show these general effects and quantify the magnitude of the various interactions.

Numerical simulations of cell pressure velocity in the cap, and chemical flux rate were performed with IBM Continuous System Modeling Program. Equations (4), (8), and (10) were the primary model equations and were solved simultaneously. Benzene was used as the test chemical in all simulations. Table 1 lists the base case for simulation along with landfill and other parameters. The parameters headed *Physical and chemical* were held constant for all simulations.

The primary forcing function that drives the so-called barometric pressure pumping mechanism is the variation in atmospheric pressure with time $\pi(t)$. Barometric pressures recorded at Fayetteville, Arkansas spanning the two week period of February 22 through March 7, 1980 were used for $\pi(t)$. During this two week period atmospheric pressure cycled three times; high pressures in the cycles were 30.52, 30.57, and 30.22 inches of mercury while the corresponding low pressures were 29.81, 29.88, and 29.64 inches.

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TABLE 1

Landfill, physical and chemical parameters

Landfill			Physical and chemical	
Variable	Base case	Range		
Permeability (darcys)	1.08	0.178-3.35	Waste density (g/cm ³)	1.5
Cap porosity	0.22	0.180-0.25	Temperature (°C)	25
Cell porosity	0.16	0.083-0.204	Gas viscosity (cp)	0.01
Bio-gas (cm ³ /g s)	2.6×10^{-7}	$0-6.5 \times 10^{-7}$	*Molecular wt. (g/mol)	78
Cell depth (m)	20	6-38	*Vapor pressure (atm)	125
Cap thickness (m)	3.5	1.35-5.0	*Diffusivity (cm ² /s)	0.001

*Benzene properties at 25°C.

These pressure cycles, which are not atypical, and a two week time period were used in all simulations.

On a longer time scale, some landfill parameters undergo significant changes. Based on the measurements Lu and Matuszek [1] performed on seven trenches containing waste, changes in cap permeability apparently varied considerably with the seasons. Table 2 contains cap permeability measurements made in twelve trenches approximately 180 m long, 10 m wide, and 6 m deep in a silty clay bed. Each trench was covered with 2 to 5 m of the excavated till.

TABLE 2

Permeability of waste trench cap

Trench	October 1977	K (darcys) February 1978	April 1978	July 1978
3	0.401	0.0852	—	0.497
5	0.696	0.312	0.0994	4.26
8	—	0.369	0.114	3.91
9	—	—	0.170	—
10	—	—	0.195	—
11	—	0.146	0.140	4.19
12	—	—	0.351	3.91
average	0.549	0.228	0.178	3.35

*Calculations based on data of Lu and Matuszek [1] with $L = 3.5$ m and $\mu = 0.018$ cp.

The authors noted that, "the trench covers are highly permeable to pressure-induced flow of gas and air. It appears that a network of fractures play a dominant role in the rate of flow of gases from the trenches. The permeability of the trench covers appears to be dramatically affected by

climatic conditions further north in February centimeter caused by from melt (in July 1 conditions conditions out of trench of water st Based on trenches (c The cap po openings are related to cap permeability from empirical permeability very dry common for clay seems reasonable occurred in July

$$K = ae^{\theta}$$

with $K = 3.3$ in eqn. (11)

TABLE 3

Season values of

Month	Cap con.
October	Cell. waste
February	Cap cover
April	Cap and
July	Cap dry p

climatic conditions." In explaining the seasonal differences, the authors further note that; ... "measurements were made for trenches 3, 5, 8, and 11 in February 1978, when the trench caps were frozen and covered by several centimeters of snow." ... "The low values of K (for April 1978) may be caused by infiltration of the fractures with precipitation and with water from melting snow." ... "The extraordinary changes in bulk permeability (in July 1978) of the trench cap is mainly attributed to very dry weather conditions which had existed for more than 6 weeks." The only seasonal conditions mentioned for October 1977 were: ... "Water was being pumped out of trenches 3, 4, and 5 by the site operator in order to reduce the level of water standing in the trenches".

* Based on estimated trench void volumes apparent porosities for the trenches (or cells) ranged from 0.0833 to 0.204 with an average of 0.161. The cap porosities are not so readily available. The sizes of the fracture openings and the fracture porosities are not directly observable but must be related to cap permeability. Lerman [6] suggests that the dependence of permeability on porosity be of the form $K \sim \epsilon^n$ and that $n = 9$ emerges from empirical determinations. It was noted that the extraordinary bulk permeability of the trench cap observed in July 1978 was attributed to very dry conditions which existed for more than 6 weeks. It is not uncommon for clays to display macro porosities of 27 to 33% when dry. It then seems reasonable that when the observed permeability of 3.35 darcys occurred in July, the effective porosity was likely to be 0.25. Using

$$K = a\epsilon^9 \quad (11)$$

with $K = 3.35$ and $\epsilon = 0.25$ yields $a = 878182$. Cap porosities, estimated using eqn. (11), for the observed permeabilities appear in Table 3.

TABLE 3

Season values of landfill cap permeability, porosity, and benzene diffusion coefficient

Month	Cap or cell climatic-conditions	Permeability K (darcys)	Porosity ϵ (%)	Benzene diffusion coeff., D_{A3} (cm ² /s)
October	Cells contain standing water	0.549	20.4	0.0106
February	Cap frozen with snow cover	0.228	18.5	0.00928
April	Cap very wet from rain and snow melt	0.178	18.0	0.00894
July	Cap very dry, 6 week dry period	3.35	25.0	0.0139

Molecular gas diffusivities for chemicals in porous media are modified by the presence of the solid matrix. The cross-sectional area is reduced and the diffusion path is lengthened. Farmer et al. [2] measured the effective diffusivity of hexachlorobenzene through soil layers and correlated the observations with the relation:

$$D_{A3} = D_{AI} \epsilon^{4/3} \quad (12)$$

where D_{AI} is the molecular diffusivity of species A in air. Investigations in our laboratory (Ballard et al. [7]) with methanol, ethanol, and isopropyl alcohol also indicate that eqn. (12) satisfactorily represents the data. For $D_{AI} = 0.088 \text{ cm}^2/\text{s}$ of benzene in air at 25°C , Table 3 contains the effective soil pore diffusivities calculated from eqn. (12).

The following are assumptions implicit to the above model. Pore diffusion occurs in gas phase only. The presence of water in the cap is accounted for through the porosity; however, water movement and associated chemical movement is not quantified. Thermal gradients are assumed to have no effect on the chemical flux rate. Absorption or partitioning of the chemical in the soil or pore water is neglected. All diffusion resistance is assumed to be in the soil and none in the air boundary layer. Air which enters the cells is assumed to come into contact with and to equilibrium with the liquid and/or solid material that contains hazardous chemicals.

Simulation results

Parameters for the "base-case" listed in Table 1 were chosen to represent a typical landfill that contains both chemical waste and/or conventional solid waste. Benzene was chosen to represent the hazardous chemical and the presence of solid waste is reflected through a finite bio-gas generation rate. The base-case simulation serves as a standard for comparison in studies of mechanisms and parameter sensitivity. Integration was performed by the Runge-Kutta method with a step size of 0.0005 d. A copy of the IBM continuous system modeling program is available upon request.

The dynamic behavior of internal pressure, p , and flux, n_A , in the base case for a two week simulation period is shown in Fig. 3. This simulation corresponds to a combined landfill with significant internal gas generation. The flux rate of benzene through the cap, n_A , is influenced slightly by barometric pressure. R varies between 4.4 and 13.0 indicating that gas flow through the pores in the cap is the dominant mechanism of emission. The emission rate (2 wk. ave.) is $117 \text{ g/m}^2 \text{ d}$. It is apparent from this calculation that the typical combined waste landfill will not readily retain benzene. Fifty-five gallons (183 kg) of benzene placed in a cell of 100 m^2 surface area has a residence time of 15.7 days at this rate.

A hazardous waste landfill should not contain quantities of materials that generate gas in the cells. Figure 4 is the p and n_A dynamic behavior for

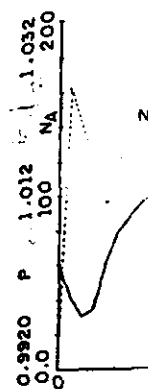


Fig. 3. $P(\text{atm})$

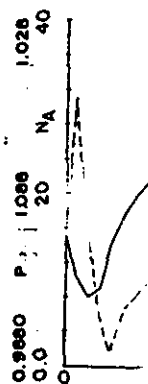


Fig. 4. $P(\text{atm})$

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in air. Investigations of ethanol, and isopropyl alcohol, presents the data. Figure 3 contains the effective

ve model. Pore diffusion in the cap is accounted for and associated elements are assumed to be for partitioning of diffusion resistance in the layer. Air which is in and to equilibrium with hazardous chemicals.

are chosen to represent and/or conventional hazardous chemical and its bio-gas generation or comparison in simulation was performed by the copy of the IBM computer request.

flux, n_A , in the barometer. Fig. 3. This simulation of internal gas generation is influenced slightly by indicating that gas flow is a function of emission. The amount from this calculation is likely to retain benzene. All of 100 m² surface

amounts of materials in dynamic behavior for

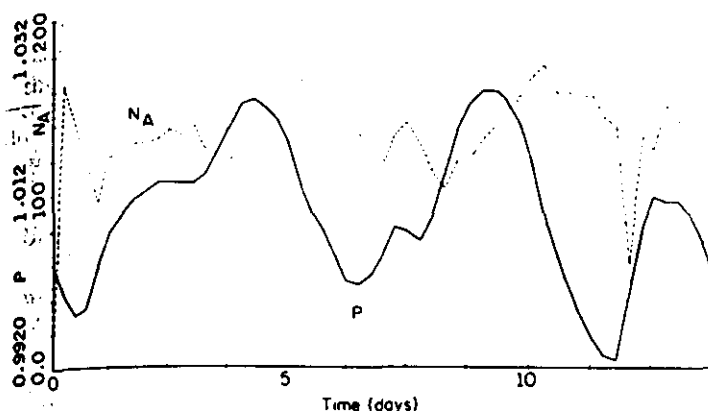


Fig. 3. $P(\text{atm})$ and $N_A(\text{ng/s cm}^2)$ simulation with bio-gas generation;

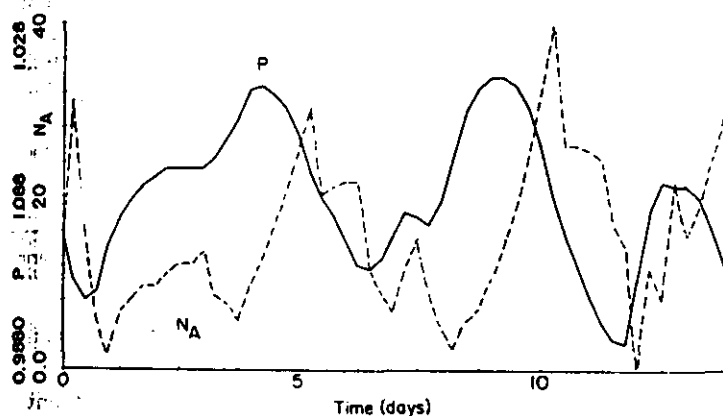


Fig. 4. $P(\text{atm})$ and $N_A(\text{ng/s cm}^2)$ simulation without bio-gas generation.

simulation without gas generation. The flux is also influenced significantly by barometric pressure. The two week average emission rate falls to 13.0 g/m² d. One drum under 100 m² surface area will evaporate completely in 140 days. The lack of gas generation reduces the emission rate significantly but does not eliminate it. R for this case varied between -5.8 to 2.8 indicating that the emission was diffusion controlled.

It is interesting to study the role barometric pressure fluctuations have on the emission rate. A simulation with atmospheric pressure constant at 1.00 atm for two weeks yields a flux of 11.5 g/m² d and $R = 0$. It therefore appears that the fluctuations of barometric pressure can increase the pure diffusion emission rate by approximately 13%. The above results are summarized in Table 4A. All fluxes in Table 4 are two week averages.

TABLE 4

Average benzene emission rates — simulation results

Mechanism or parameter of study	Value	Emission (g/m ² /d)	
		Bio-gas	No-gas
A. Mechanism	Diffusion, bio-gas, and atm. press.	117*	—
	Diffusion and bio-gas generation	115	—
	Diffusion and atmospheric press. pump	—	13.0
	Diffusion only	—	—
B. Season	October ($\epsilon = 0.204$)	116	12.0
	February ($\epsilon = 0.185$)	116	10.8
	April ($\epsilon = 0.180$)	115	10.5
	July ($\epsilon = 0.250$)	117	15.0
C. Cover thickness, L (m)	1.35	119	30.4
	3.50	117	13.0
	5.0	117	10.1
	—	117	11.9
D. Cell porosity, ϵ_c	0.0833	117	11.9
	0.16	117	13.0
	0.204	116	13.9
	—	—	—
E. Cell depth, h_c (m)	6.0	36.9	11.6
	20.0	117	13.0
	38.0	221	16.4
	—	—	—
F. Bio-gas r_B (cm ³ /g s)	0.0	—	13.0
	$2.6E-7$	117	—
	$6.5E-7$	292	—
	—	—	—
G. Low cover porosity (ϵ)	0.100	—	3.90

*Base case includes molecular diffusion, bio-gas generation sweep effect and atmospheric pressure pumping.

With the field cap permeability observations of Lu and Matuszek [1], it is possible to estimate the effect the seasons of the year may have on the emission rate. Table 3 contains the seasonal climatic conditions and pertinent cell cap parameters. The results appear in Table 4B. When bio-gas generation within the cells is constant at a rate of 2.6×10^{-7} cm³/g s, the benzene flux rate shows little seasonal dependence. A seasonal dependence may be noticeable if temperature affects reaction time. The model in its present form does not account for seasonal temperature changes within the cell waste material. If no bio-gas is generated, then the benzene emission rate is effected by changes in cap parameters. Significant increases in flux rate (43%) occur from April when the cap is wet, to July when the cap is dry.

Cap cover thickness is thought to be an effective means of reducing vapor emissions from landfills. The simulation model suggests that when bio-gas is generated, increased cover thickness has no effect (see Table 4C). If no bio-gas is present, the increased cap thickness is effective in reducing the emission rate of toxic vapors.

It appears that cell properties of porosity and depth have a slight effect on emission rate. Table 4, D and E, suggests that increases in both of these

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Emission (g/m ² /d)	Bio-gas No.
117*	—
115	—
—	13.0
116	12.0
116	10.8
115	10.5
117	15.0
119	30.4
117	13.0
117	10.1
117	11.9
117	13.0
116	13.9
36.9	11.8
117	13.0
221	16.4
—	13.0
117	—
292	—
—	3.90

ect and atmosphere

Matuszek [1] have on the emissions and pertinent bio-gas generation rate, the dependence of the model in its present form within the cell, the emission rates in flux rate, the cap is dry, the effect of reducing the tests that when (see Table 4C), the effect in reducing

have a slight effect in both of the

parameters increase emission rate slightly. Table 4F shows that emission rate increases proportionally with increased bio-gas rate and Table 4G shows that a low cover porosity of 0.10 can significantly reduce the emission rate. The residence time for one drum under a 10 m X 10 m surface is 1.29 years. A low cap permeability will not stop emissions but it will reduce the rate.

Uncertainties and limitations of the model

The model developed above is very theoretical but does provide a framework for future models which will take into account more realistic features of the cell system. The model assumes free circulation of vapor/gas/air around particles of the offending liquid or solid. In current practice the liquid will eventually escape from its container and be adsorbed onto a solid. The aspect of adsorption is not taken into account in the model as it is presented. Free circulation of gases within and between cells is also not accounted for. Both these aspects can be taken into account by logical extensions of the basic model concept.

The model shows that the most significant case is where biogas is produced. This is precisely the case where absorption onto solids will be most relevant. The work of Jones et al. [8] shows the sorption from aqueous solution onto biodegradable waste reduces the source term by a factor of between 10–100 for several volatile solvents. Presumably a similar partitioning will occur between vapor spaces and solid/liquid phases that may reduce the pore-space concentration. This effect can be accounted for by applying the appropriate partition coefficient for sorption which effectively reduces ρ_{AJ} appearing in eqn. (8).

At present the model includes only a single-celled landfill. More realistic simulation of landfills consisting of multiple cells can be achieved by applying the concepts to the individual cells and interconnecting chemical transfer between cells. This extension to an n -cell system will result in n differential equations such as eqn. (10) and a more realistic simulation. In a multi-layered landfill chemical concentration gradients exist between the lower cells and the upper cells. The refined n -cell system model will incorporate this feature and allow for varying degrees of cell waste compaction with depth, etc. The third generation model should also include a source term since the quantity of volatile material placed in each cell is finite. Anaerobic reaction of key chemical species should also be included as a sink term in the species mass balance of each cell.

Conclusions

A dynamic model has been developed to simulate the transport of toxic vapors from cells of hazardous waste landfills, through the cap material and into the overlying air. Using benzene as a test chemical the following conclusions can be made.

1. All three mechanisms: bio-gas generation, atmospheric pressure pumping and molecular diffusion, contribute to the gas-phase transport of chemical species to the air.
2. When biodegradable waste is present internal gas generation is the dominant mechanism. Flux rates through the cap of 37 to 290 g Benzene/m² d were calculated. However, chemical adsorption onto bio-solids may reduce these flux rates significantly.
3. When no bio-gas is produced within the cells molecular diffusion is the dominant mechanism. Flux rates were 11 to 30 g/m² d. Atmospheric pressure fluctuations enhanced molecular diffusion by about 13% for benzene.
4. Studies of parameter sensitivity using the model suggest that cap porosity is the most critical parameter for controlling vapor emission rates. A clay cap with 10% porosity and 3.5 meters thick will reduce the emission rate to 3.9 g Benzene/m² d.
5. This and previous emission models suggest that there is an urgent need for experimental work to provide field data to serve as a guide for future theoretical work.

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PROPAGATION MIXTURE

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